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HEXAKIS(ANILINE)PHTHALOCYANINATOIRON(II), HEXAKIS(ANILINE-D7)
JUN 77 C K CHOY, J R MOONEY, M E KENNEY N00014-75-C-0693

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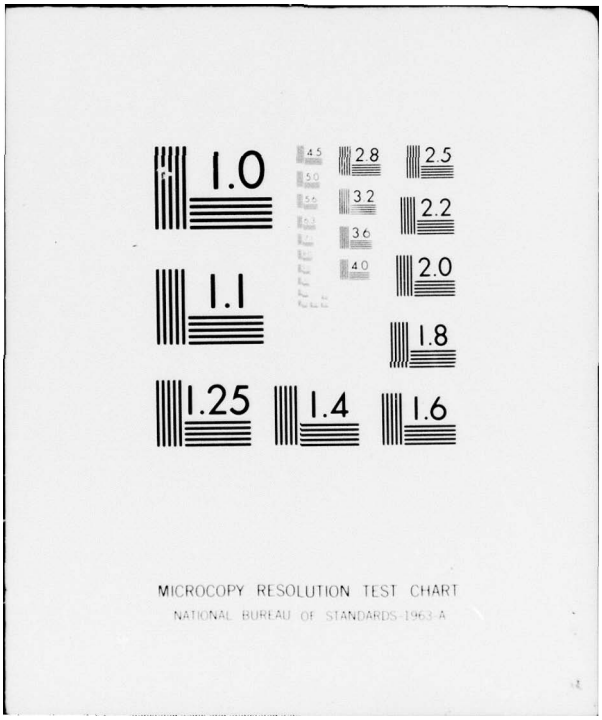
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(6) # HEXAKIS(ANILINE)PHTHALOCYANINATOIRON(II), HEXAKIS(ANILINE-d_7)-PHTHALOCYANINATOIRON(II), AND OTHER RELATED HIGHLY SELECTIVE NMR SHIFT REAGENTS.

(14) TR-2

by

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(11) 14 June 77 (12) 17 p.

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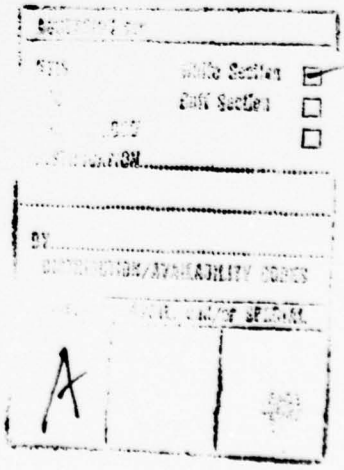
ABSTRACT

The significant properties of three good iron(II) phthalocyanine nmr shift reagents, FePc, $FePc(NH_2C_4H_9)_2$, and $FePc(ND_2C_4D_9)_2$ and two superior shift reagents of the same type, $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$ are described and discussed. Some of the kinds of compounds the latter two generally can be expected to function with and some of the kinds of compounds they generally can be expected not to function with are given, i.e., imidazoles, pyridines, pyrrolidenes, and primary aliphatic amines; and pyrroles, secondary aliphatic amines, tertiary aliphatic amines, aromatic amines, alcohols, ethers, and many other compounds carrying oxygen functions, respectively. Where they can be clearly identified, properties of these compounds which are important to the behavior they show toward the reagents are alluded to. Throughout the value of the selectivity which the reagents show with both monofunctional and polyfunctional compounds is emphasized.

Running Head: Phthalocyaninatoiron(II) Shift Reagents



INTRODUCTION

Previous work has shown that a group of diamagnetic metal porphyrin and metal phthalocyanine complexes function as effective nmr shift reagents (1-4). These reagents owe their ability to act solely to the ring currents of their rings; the metal ions in them, iron(II), cobalt(III), ruthenium(II), lutecium(III), silicon(IV), and germanium(IV), all being diamagnetic.

The iron reagents of this group are of the phthalocyanine type and show, as do apparently most or all of these reagents, marked selectivity in their action. This makes these reagents attractive from a variety of standpoints.

In the present paper, work on a group of the iron reagents is described. Special emphasis is given to $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$ (Pc = the phthalocyanine ligand, $C_{32}H_{16}N_8$) since these reagents have been found to possess a particularly advantageous set of properties.

EXPERIMENTAL

Shift Reagents: FePc. The iron(II) phthalocyanine used was purchased (Eastman).

$FePc(NH_2C_4H_9)_2$ (5). In an apparatus allowing flask-to-flask vacuum distillation, n-butylamine (10 ml) was vacuum distilled onto FePc (1.0 g) and the suspension thus produced was stirred for 8 hr. The resultant was reduced in volume by distilling off much of the excess amine ($\sim$ 8 ml), then was mixed with a 1:1 benzene-pentane solution and filtered. The product, a dark blue solid, was washed and vacuum dried (1.2 g). An nmr spectrum of it indicated it was the sought-after compound accompanied by a small amount of amine.

The compound was also produced by the reaction of FePc and excess amine in ordinary apparatus, recovered by evaporation of the excess amine, and purified by recrystallization.

$FePc(ND_2C_4D_9)_2$. Using the flask-to-flask technique described for the synthesis of $FePc(NH_2C_4H_9)_2$, n-butylamine-d_9 (Merck) and FePc were reacted together and the resultant product isolated. An nmr spectrum of this product showed that its butyl groups had very high isotopic purity and that its amino groups had reasonably high isotopic purity.

$FePc(NH_2C_6H_5)_6$ (6). Following Linstead, a mixture of FePc (1.0 g) and aniline (12 ml) was refluxed for 1 hr. The resultant was filtered and the filtrate, a deep green solution, was cooled slowly for 12 hr. The product, a mass of beautiful dark-purple crystals, was recovered by filtration, washed, and dried (0.80 g).

$FePc(ND_2C_6D_5)_6$. Using the zinc-acid technique for reducing nitrobenzene to aniline (7), nitrobenzene-d_5 was reduced to aniline-d_5. This was equilibrated repeatedly (4x) with deuterium oxide. The aniline-d_7 thus obtained and FePc were then reacted and the product was isolated using a procedure analogous to that described for $FePc(NH_2C_6H_5)_6$.

The reagent was also prepared from commercial aniline-d_7 (Merck).

Shift Complex Solutions -- FePc. The technique used to prepare a solution of the shift complex of a compound produced by FePc was straightforward. First the complex was synthesized and isolated by conventional means, then a small amount of it ($\sim$ 1-5 mg) was dissolved in deuterochloroform ($\sim$ 0.5 ml), and finally, if appropriate, the solution was filtered.

The procedures used to make up and isolate the shift complexes of N-methylimidazole and γ-picoline are typical of those used to prepare the complexes. $FePc(NC_3H_3NCH_3)_2$ (8). A mixture of FePc (0.50 g), N-methylimidazole (1.0 ml) and benzene (100 ml) was refluxed for 6 hr. and filtered.

The filtrate, a deep green solution, was brought to reflux, cooled slowly, and filtered. The product, large rough-surfaced purple crystals, was filtered off and washed (100 mg). It was then crushed, washed, and dried. Anal. Calcd. for $C_{40}H_{28}N_{12}Fe$: C, 65.58; H, 3.85; Fe, 7.62. Found: C, 65.70; H, 4.04; Fe, 7.75. $FePc(NC_5H_4CH_3)_2$ (9). With the aid of an extraction apparatus designed to permit the extraction of a solid at the reflux temperature of the solvent being used, PcFe (200 mg) was subjected to the action of refluxing γ-picoline (10 ml) for 36 hr. The resultant suspension was cooled slowly and filtered. The product, purple crystals, was washed and air dried (100 mg). It was then vacuum dried. Anal. Calcd. for $C_{44}H_{30}N_{10}Fe$: C, 70.03; H, 3.97; Fe, 7.50. Found: C, 69.93, 70.11; H, 3.75; Fe, 7.30.

$FePc(NH_2C_4H_9)_2$, $FePc(ND_2C_4D_9)_2$, $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$. The technique used to prepare a solution of the shift complexes of a compound produced by $FePc(NH_2C_4H_9)_2$, $FePc(ND_2C_4D_9)_2$, $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$ was very simple. One or more crystals of the reagent (∿ 1-5 mg) were dissolved in a solution of the compound (∿ 1-5 mg) in deuterochloroform (∿ 0.5 ml) and, if appropriate, the resultant solution was filtered.

Instruments -- The spectrometers used were Varian HA-100 and XL-100-15 instruments. They were operated in F.T. mode.

RESULTS AND DISCUSSION

Features of Reagents -- Each of the reagents possesses both good and bad features. A good feature of the simplest of them, FePc, is that it gives spectra which are quite simple. These contain resonances from the phthalocyanine ring (a low field AA'BB' multiplet) and from the compound of interest in its bound and sometimes its free form. The key resonances, those from the compound in its bound form, are generally well separated and not overlapped with any free compound resonances present.

A second good feature of FePc is its commercial availability. A third is its stability.

On the other hand, the use of this reagent does require relatively large amounts of the compound (and of it). Further, and for many purposes more important, use of it requires two sets of manipulations.

The nondeuterated butyl reagent which functions, as is obvious, by an exchange mechanism, is good because its use requires only a small amount of the compound and of it, and only a single set of manipulations. However, it does give spectra which are more complicated. These contain resonances (of varying relative intensities) from the phthalocyanine ring, from butylamine in both its free and bound forms, and from the compound of interest in its free and bound forms. The resonances from the phthalocyanine ring, the butylamine in its bound form, and the compound of interest in its bound form, occur in sets (because the solution produced by the reagent contains $FePc(NH_2C_4H_9)_2$, $FePc(NH_2C_4H_9)$(compound), and $FePc(compound)_2$ but usually only one signal for each set is observed and hence the spectra, while somewhat cluttered, are not difficult to deal with.

The deuterated reagent is similar to its nondeuterated analog except that it gives spectra lacking butyl resonances (to the extent its butyl groups are isotopically pure) and thus it gives less cluttered spectra. It is, though, much more expensive than its analog.

As with the butyl reagents, the nondeuterated aniline reagent is good in that only a small amount of it is needed, only a small amount of the compound is needed, and only a single set of manipulations is needed. The spectra it gives contain resonances from the phthalocyanine ring, from free aniline, and from the compound of interest in its free and bound forms. Accordingly, the spectra it gives are much more desirable than those from the nondeuterated butyl reagent.

The deuterated aniline reagent is superior to its analog in that it gives spectra free of phenyl resonances (to the extent its phenyl groups are isotopically pure). Balancing this in part is the greater effort (or alternatively cost) associated with its synthesis.

Both it and its nondeuterated analog have the advantage of generally giving spectra in which the bound compound resonances are relatively strong. In addition, both are easy to handle and store. (While it is known from Linstead's work that the nondeuterated reagent loses aniline on standing (6), the loss of aniline by the reagents poses no practical problem.)

As is to be expected, other similar amine reagents can be used besides the ones just described. For example, the complexes of isopropylamine, γ-picoline, and neopentylamine all can be used as reagents. However, no reagents superior to those already described have been found (the problem with the isopropyl reagent is its low stability, that with the pyridine reagent its high stability, and that with the neopentyl reagent the intensity of the bound and free neopentyl resonances it gives).

As far as is known FePc, the two butylamine reagents, and the two aniline reagents all work with the same types of amines. Considering this and the various other factors, the two aniline reagents are the reagents which, in general, can be expected to be the ones of choice.

Based on the results of a number of experiments, the behavior of these two reagents can be projected with confidence with certain types of heterocyclic amines, with aliphatic amines in general, and with aromatic amines in general. Their behavior with a number of other types of compounds such as ethers, alcohols, etc. can also be projected with confidence.

Behavior of Aniline Reagents -- Imidazoles. With imidazoles, a very important group of heterocyclic amines, the aniline reagents in general can be expected to function well. (Often the spectra they yield with amines of this type contain a small broad extraneous resonance in the vicinity of the phthalocyanine resonances, but this does not interfere and causes no difficulty.)

One imidazole with which both reagents have been shown to work very nicely is, Table 1, N-benzylimidazole. A second with which the deuterated reagent has been shown to work is 1-ethyl-5-phenylimidazole. (The sample of this compound used was the generous gift of Prof. Ray A. Olofson of the Pennsylvania State University.)

In functioning with imidazoles the reagents clearly react with the pyridine-like nitrogens. The stability of the bond formed can be ascribed in part to a contribution from π bonding. As is to be expected the reagents do not function with imidazoles hindered at N-3. A case in point is 1,2-dimethylimidazole, Table 1. Another is almost certainly 4(5)-phenylimidazole.

Pyridines. The reagents generally can be expected to work well with pyridines also. A pair of pyridines with which the deuterated reagent is known to work well is that listed in Table 2. Since isoquinoline is a pyridine with which FePc works, both reagents will also certainly work with this amine.

As with the imidazoles, part of the strength of the Fe-N bond formed can be ascribed to π-bonding. It is to be expected,naturally, that the reagents will not work with hindered pyridines such as quinoline.

Pyrroles. The reagents can be expected, as a rule, to fail to function with pyrroles, one of the reasons for this being the lack of fully free, appropriately oriented electron pairs on their nitrogens. As indicated, the nondeuterated reagent does not work with pyrrole, itself.

Pyrrolidines. In contrast to the case with pyrroles, the reagents can be expected to work well with a variety of unhindered pyrrolidines. One such compound with which the nondeuterated reagent does work is pyrrolidine itself.

Primary aliphatic amines. It can be assumed that the reagents will work well with most primary aliphatic amines, e.g., n-hexylamine. That steric effects can prevent the reagents from working is shown by the case of 1-adamantylamine.

Secondary aliphatic amines. With most secondary aliphatic amines, because of steric effects, it is thought that the reagents will be ineffective. An amine of this type with which the nondeuterated reagent is ineffective is di-sec-butylamine. However, with secondary amines which are relatively unhindered, they can be expected to be effective. As already mentioned, the nondeuterated reagent works with pyrrolidine, one such amine.

Tertiary aliphatic amines. Again because of steric effects, it is thought that the reagents will be ineffective with nearly all tertiary aliphatic amines.

Aromatic Amines. With essentially all aromatic amines, it is anticipated that the reagents will be ineffective.

Diamines. With those diamines with which they can work, the reagents can often be expected to react predominantly or solely with just one of the two functions. For example, with 1-amino-2-diethylaminoethane the deuterated reagent reacts only with the primary function. Similarly with 4-aminomethylpyridine the deuterated reagent reacts only with the pyridyl function (it appears that the reagents form particularly stable shift complexes with pyridyl and imidazole functions).

Even with diamines with identical functions the reagents can often be anticipated to interact predominantly or sometimes even essentially solely with just one of the functions under favorable conditions. Thus the non-deuterated reagent reacts essentially with only one of the amino groups of propylenediamine when the reagent to amine ratio is high, Figure 1. (When the ratio is low the reagent reacts with both groups and forms oligomeric species.) Other diamines with which one or the other of the two reagents react selectively are ethylenediamine, hexamethylenediamine. and octamethylenediamine, Table 2.

Isomeric amines. Where one of a pair of isomeric amines belonging to one of the classes with which the reagents will react is hindered and the other is not, the reagents can be expected to work selectively. For example, the reagents can be expected to function with 1,5-substituted imidazoles but

not with their 1,4 isomers (the fact that the reagents can be expected to act thus and accordingly can be expected to allow the differentiation of 1,4 and 1,5 imidazole isomer pairs is of some importance because the distinction of such pairs by ordinary techniques is difficult (10)).

Other Compounds. With compounds carrying many common oxygen functions it can be anticipated that the reagents will not work. Evidence for this is seen in the data on the oxygen containing compounds presented in Table 2.

Two less common kinds of compounds they may on occasion function with, based on Balch's, (8), Taube's (11) and Stynes'(12) work, are isonitriles and nitroso aromatics.

CONCLUSIONS

The aniline reagents are the best of the iron phthalocyanine shift reagents for most purposes. They can be expected to interact with certain types of amines and not with others nor with a variety of common nonamine bases and hence to act highly selectively both with monofunctional and polyfunctional amines. They can be expected in general to give complexes of specific stoichiometry, two amines to one iron phthalocyanine, and specific geometry, trans, and hence to yield spectra with predictable and easily understandable shifts. In practice they are easy to make, simple to store, and uncomplicated to use.

Acknowledgment

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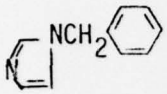
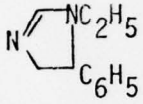
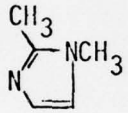
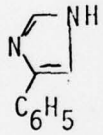
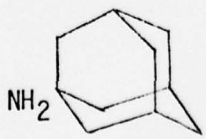
TABLE 1

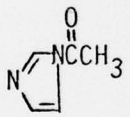
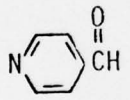
SIMPLE AMINES WITH ANILINE REAGENTS

Type	Amine	Reagent	Applicability[a]
imidazole		D,H	F
		D	F
		H	N
		H	N
pyrrole		H	N
pyrrolidine		H	F
primary	$NH_2(CH_2)_5CH_3$	H	F
		H	N
secondary	$NH(CHCH_3C_2H_5)_2$	H	N

[a] F = fully applicable; N = not applicable

TABLE 2

POLYFUNCTIONAL COMPOUNDS WITH ANILINE REAGENTS

Functions		Compound	Reagent	Selectivity[a]	Active Functions
$-NH_2$			D	F	
≡N	$-NH_2$	$NH_2CH_2CH_2N(CH_2CH_3)_2$	D	F	NH_2
$-NH_2$	$-NH_2$	$NH_2(CH_2)_2NH_2$	H	P	both NH_2
		$NH_2(CH_2)_3NH_2$	H	P	both NH_2
		$NH_2(CH_2)_6NH_2$	D	P	both NH_2
		$NH_2(CH_2)_8NH_2$	H	P	both NH_2
			D	F	
			D	F	
-OH	$-NH_2$	$NH_2(CH_2)_6OH$	D	F	NH_2
-OH -O-	$-NH_2$	$NH_2(CH_2)_3(OCH_2CH_2)_2OH$	D	F	NH_2

[a] F = fully selective; P = partially selective

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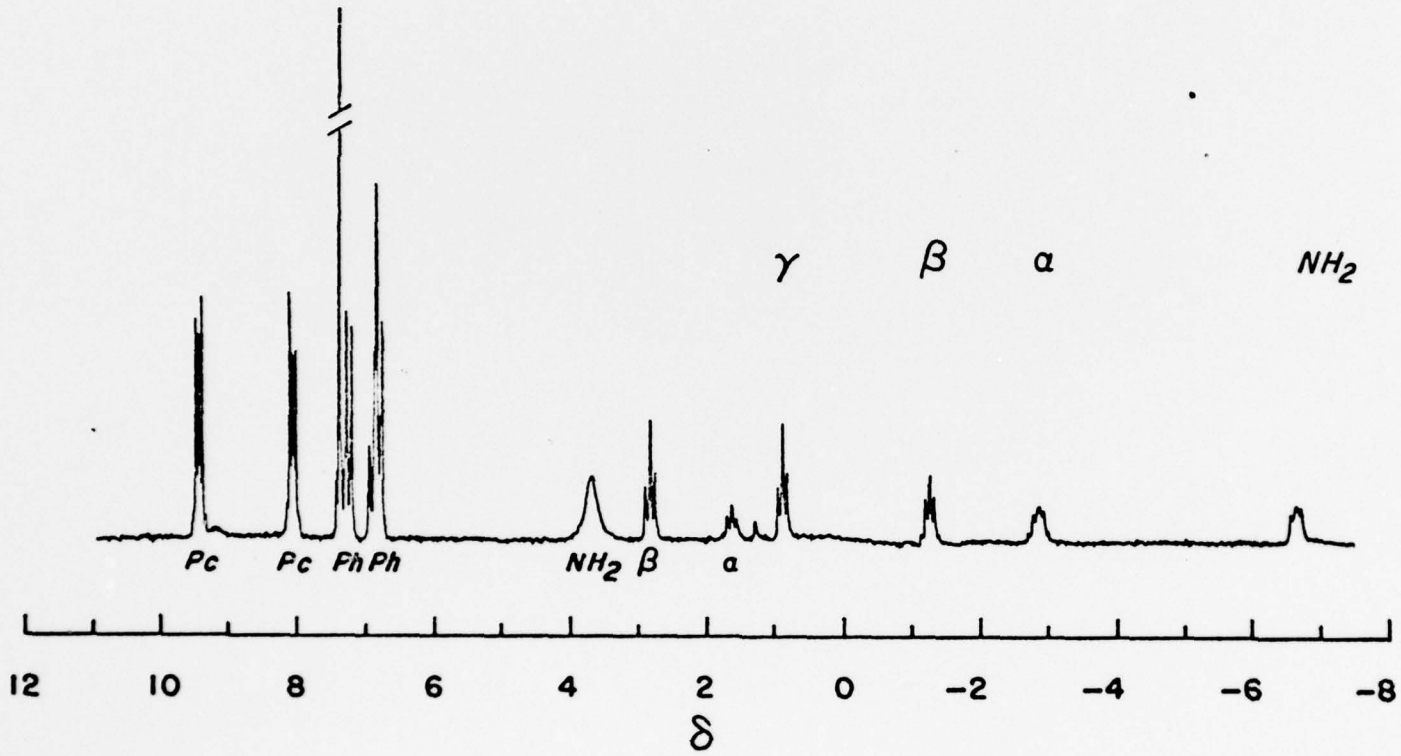

Figure 1. The spectrum of propylenediamine in the presence of the shift reagent $FePc(NH_2C_6H_5)_6$.

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19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Nuclear Magnetic Resonance Spectroscopy, Shift Reagents, Phthalocyanines, Iron, Amines

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The significant properties of three good iron(II) phthalocyanine nmr shift reagents, FePc, $FePc(NH_2C_4H_9)_2$, and $FePc(ND_2C_4D_9)_2$ and two superior shift reagents of the same type, $FePc(NH_2C_6H_5)_6$ and $FePc(ND_2C_6D_5)_6$ are described and discussed. Some of the kinds of compounds the latter two generally can be expected to function with and some of the kinds of compounds they generally can be expected not to function with are given, i.e., imidazoles, pyridines, pyrrolidenes, and primary aliphatic amines; and pyrroles, seconday aliphatic

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20. (cont.) amines, tertiary aliphatic amines, aromatic amines, alcohols, ethers, and many other compounds carrying oxygen functions, respectively. Where they can be clearly identified, properties of these compounds which are important to the behavior they show toward the reagents are alluded to. Throughout the value of the selectivity which the reagents show with both monofunctional and polyfunctional compounds is emphasized.